

Impact of declining atmospheric deposition on forest soil solution chemistry in Flanders, Belgium

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HIGHLIGHTS

- Acidifying depositions were related to soil solution chemistry in Flanders forests.
- Depositions of N and S decreased significantly between 1994 and 2010.
- Lichen and ground vegetation based critical loads for N were still exceeded.
- Critical limits for BC/Al and ANC were exceeded and soil acidification continued.
- Recovery is delayed by soil buffering processes and decreasing BC depositions.

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ABSTRACT

Throughout Europe and the USA, forest ecosystem functioning has been impacted by long-term excessive deposition of acidifying compounds. In this study, we report on trends in stand deposition and soil solution fluxes of inorganic nitrogen (N) and sulphur (S) compounds over a 17-year period (1994–2010) in five ICP Forests monitoring plots in Flanders, northern Belgium. Deposition was dominated by N, and primarily NH_4^+ . Deposition of SO_4^{2-} and NH_4^+ declined by 56–68% and 40–59% respectively. Deposition of NO_3^- decreased by 17–30% in deciduous forest plots, but remained stable in coniferous forest plots. The decrease of N and S deposition was paralleled by a simultaneous decline in base cation ($\text{BC} = \text{Ca}^{2+} + \text{K}^+ + \text{Mg}^{2+}$) deposition, resulting in a 45–74% decrease of potentially acidifying deposition. Trends in soil solution fluxes of NH_4^+ , NO_3^- , SO_4^{2-} and BC mirrored declining depositions. Nitrate losses below the rooting zone were eminent in both coniferous forest plots and in one deciduous forest plot, while net SO_4^{2-} release was observed in two deciduous forest plots. Critical limits for BC/Al ratio were exceeded at the three plots on sandy soils with lower cation exchange capacity and base saturation. Soil solution acid neutralizing capacity increased but remained negative, indicating that soil acidification continued, as the start of recovery was delayed by a simultaneous decrease of BC depositions and short-term soil buffering processes. Despite substantial reductions, current N deposition levels still exceed 4–8 times the critical load for safeguarding sensitive lichen species, and are still 22–69% above the critical load for maintaining ground vegetation diversity.

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1. Introduction

Since the late 1970s atmospheric deposition of sulphur (S) and nitrogen (N) has been related to adverse effects on forest soil condition and soil solution chemistry throughout Europe and the

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USA (Aber et al., 1989; Alewell et al., 2000; Driscoll et al., 2003; MacDonald et al., 2002; Monteith et al., 2007; Ulrich et al., 1979). According to these studies, soil acidification entailed elevated aluminium (Al) concentrations in soil solution, depletion of base cations from the soil exchange complex, diminished leaching of dissolved organic carbon following decelerated litter decomposition, and N saturation indicated by losses of NO_3^- below the rooting zone.

As soon as harmful effects of transboundary air pollution were recognized, abatement strategies were outlined within the Convention on Long-Range Transboundary Air Pollution (CLRTAP)

of the United Nations Economic Commission for Europe (UNECE) (www.unece.org). The implementation of the so-called S protocols (Helsinki 1985, Oslo 1994) and the Gothenburg multi-pollutant protocol (1999) resulted in a reduction of sulphur dioxide (SO₂) emissions in Western Europe by a factor 8–9 between 1980 and 2010, whereas emissions of nitrogen oxides (NO_x) and ammonia (NH₃) were reduced by 40% and 36% respectively (EEA, 2011; Granier et al., 2011). In Flanders, northern Belgium, emissions and depositions of potentially acidifying N and S compounds were reduced between 1990 and 2010 with respectively 61% (VMM, 2011) and 51% (Van Steertegem, 2012). Despite these reductions, current NO_x emissions in Flanders still exceed the 2010 ceilings set by European legislation (EC, 2001).

Several studies highlighted the unfavourable condition of forest soils in Belgium as a result of long-term excessive N and S depositions. A European study on ICP forests monitoring sites in several countries, including Belgium, revealed that critical limits for N concentrations in soil solution were frequently exceeded between the early 1990s and 2006 (Iost et al., 2012). Two coniferous forest plots in Flanders showed a steady decline of soil solution acid neutralizing capacity (ANC) and of molar Ca²⁺/Al ratio between 1992 and 1997, despite decreasing depositions (Neirynck et al., 2002). Over a longer period, a significant acidification of the upper layer (0.3–0.4 m) of several forest soil types was observed between 1950 and 1985 (Ronse et al., 1988). A follow-up study showed an ensued acidification of the mineral topsoil from podzols between 1985 and 2000 (De Schrijver et al., 2006).

Long-term monitoring of acidifying depositions and soil solution concentrations provides a valuable tool to evaluate abatement strategies and to track possible chemical recovery from long-term inputs. Flanders is participating in the ICP Forests programme (www.icp-forests.org), launched in 1985 under the CLRTAP of the UNECE. Data for stand deposition and soil solution chemistry in five ICP Forests monitoring plots are collected since 1994. Long-term records were analysed in order to: 1) evaluate trends in potentially acidifying depositions between 1994 and 2010, 2) investigate the effects of potentially acidifying depositions on soil solution chemistry, and 3) discuss the observed trends in relation to critical loads and levels.

2. Materials and methods

2.1. Study area

Five plots of the ICP Forests intensive monitoring network (Level II) in Flanders, northern Belgium, were included in this study (Fig. 1). Flanders has a moderate Atlantic climate with an annual precipitation of 852 mm and a temperature of 10.5 °C (long-term average for 1981–2010, data of the Royal Meteorological Institute of Belgium, www.meteo.be). Plots were circular with an area of 0.25 ha. Relevant site and soil characteristics are listed in Tables 1 and 2. Two plots are located in coniferous forest: *Pinus sylvestris* L. in Brasschaat (BRA) and *Pinus nigra subsp. laricio* (Poiret) Maire in Ravels (RAV). Both stands are situated in the northern Campine region on poor sandy soils with low base saturation. The soil profile in RAV is well-drained, while in BRA the infiltration of water is locally slowed down by clay lenses at 50–125 cm depth. Three other plots are installed in deciduous forest: *Fagus sylvatica* L. in Wijnendale (WIJ) and Hoeilaart (HOE), a mixture of *Quercus robur* L. and *F. sylvatica* L. in Gontrode (GON). WIJ is located in the western part of Sandy Flanders, on a poor sandy soil with presence of clay below 90 cm depth, a shallow groundwater table, moderately low base saturation in the mineral soil and slightly higher base saturation in the topsoil. HOE is located in the central hills of Flanders on a loamy loess soil, with moderately low base saturation and deep groundwater table (>30 m). GON is located on the slopes of a brooklet valley in the Dender-Klein Brabant ecoregion and has a moderately well-drained, sandy loam soil, overlaying a mosaic of tertiary clayey and sandy deposits with high base saturation starting at 50 cm depth.

The five plots differ in land-use history and pollution climate. RAV and BRA were planted on former heathland, WIJ on former arable land, while GON and HOE are old growth, permanently forested sites. BRA is located at 10 km from the port of Antwerp, which emits more than half of the SO₂ emissions in Flanders. Regarding NH₃ emissions RAV, BRA, WIJ and GON are more exposed, as these plots are situated in areas with intensive animal husbandry. The plots BRA, GON and HOE are located few kilometres away from major motorways, resulting in higher exposure to NO_x emitted by road transport. HOE is the most sheltered plot as it is

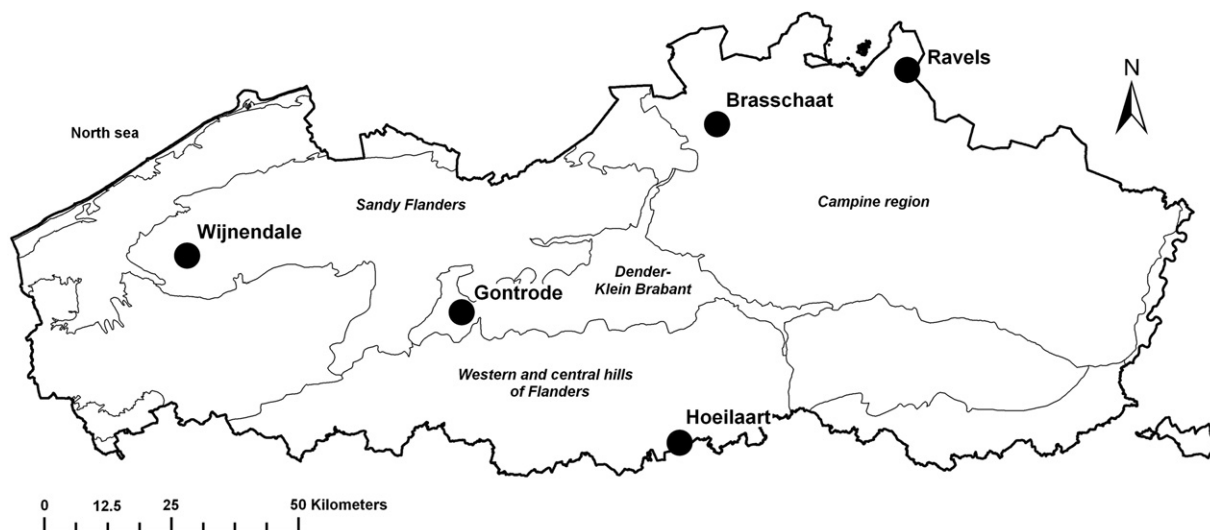


Fig. 1. Location of the five intensive monitoring plots in relation to ecoregions in Flanders (after Sevenant et al., 2002).

Table 1
Characteristics of five intensive monitoring plots in Flanders. Temperature and rainfall data are long-term averages (1981–2010, Royal Meteorological Institute of Belgium, www.meteo.be). Basal area was calculated from a full survey (DBH ≥ 5 cm) in 2009–2010. Throughfall and stemflow are expressed as the average proportion of open field precipitation.

Plot	Coordinates		Elevation (m)	T (°C)	Rain (mm)	Tree species	Planting year	Former use	Basal area (m ² ha ⁻¹)	Throughfall (%)	Stemflow (%)	Groundwater range (m)
	N	E										
Coniferous forests												
RAV	51°24'07"	05°03'15"	35	10.4	887	<i>Pinus nigra</i> subsp. <i>laricio</i> (Poiret) Maire	1930	heath	44.9	68.3		1.5–2.5
BRA	51°18'28"	04°31'11"	14	10.8	882		1929	heath	29.2	78.6		1.2–2.3
Deciduous forests												
WIJ	51°04'11"	03°02'14"	31	11.0	867	<i>Fagus sylvatica</i> L.	1935	arable	36.5	62.0	14.7	0.9–2.3
GON	50°58'31"	03°48'15"	26	10.6	786	<i>Quercus robur</i> L., <i>Fagus sylvatica</i> L.	1918	old growth	31.9	71.8	3.2	1.5–1.8
HOE	50°44'45"	04°24'47"	129	10.7	854	<i>Fagus sylvatica</i> L.	1909	old growth	28.9	70.9	5.8	>30

located inwards a 4421 ha forest complex, while the other plots are installed in smaller-scale forests (28–830 ha), making them more prone to edge-effects (Weathers et al., 2001).

2.2. Sample collection

Samples of throughfall, stemflow and soil solution were collected biweekly over the period studied (1994–2010), according to the guidelines of the ICP Forests manual (ICP Forests, 2010). Throughfall was sampled in each plot with ten systematically distributed bulk collectors. They consisted of a polyethylene funnel (14 cm Ø) placed at 1 m height, and connected to a subterranean 2 L polyethylene bottle. A nylon mesh (1 mm²) was placed in the

funnel to avoid contamination by large particles. At every sampling event, the volume collected by each collector was determined and samples were bulked together. Stemflow sampling was conducted only for *Fagus*, since stemflow for *Pinus* and *Quercus* was shown to be negligible during a preceding testing period. At each deciduous forest stand five trees of different size (mean diameter, $\pm 1\times$ and $\pm 2\times$ standard deviation of the initial tree population in 1994) were selected. Stemflow collectors consisted of flexible polyvinylchloride collars/gutters (7 cm Ø) attached horizontally to the stem at 1 m height, draining to a series of 200 L polyethylene storage containers mounted in a cascade system. The volume collected by each individual tree was determined at every sampling event. Subsamples were taken from all full containers, with subsample volumes

Table 2
Soil characteristics of five intensive monitoring plots in Flanders: Soil type according to IUSS Working Group WRB (2007). Depth, genetic horizons, C/N ratio, pH, cation exchange capacity (CEC) and base saturation (BS) for the forest floor layers (OF, OH or OFH) and 5 fixed depth layers of the mineral soil. Soil samples were analysed using methods of the ICP Forests manual (ICP Forests, 2010).

Plot	Soil type	Depth (cm)	Morpho-genetic Horizon	C/N	pH (CaCl ₂)	CEC (cmol _c kg ⁻¹)	BS (%)
RAV	Endogleyic Folic Brunic Albic Arenosol (Dystric)	–6.6 to –0.8	OF	33	2.5	23	36
		–0.8–0	OH	35	2.3	26	16
		0–5	Ap/E	27	2.9	4.6	11
		5–10	Ap/E	27	3.0	3.8	7.6
		10–20	Ap/E	23	3.1	3.6	7.4
		20–40	Bhs	21	3.4	3.3	8.2
		40–80	B, Bg1	–	4.1	1.7	15
		–5.2–0	OFH	30	2.7	25	42
		0–5	Ap1	18	3.1	2.2	18
		5–10	Ap1	18	3.2	1.8	15
BRA	Endogleyic Brunic Albic Hypoluvic Arenosol (Dystric)	0–5	Ap1	15	3.3	1.7	16
		20–40	Ap1, Ap2	14	3.4	1.6	17
		40–80	E, Bg1, Bg2	–	3.6	1.5	18
		–8.0 to –2.1	OF	25	2.7	31	42
		–2.1–0	OH	22	2.7	25	23
		0–5	A1	21	2.5	7.3	32
		5–10	A2	19	2.7	4.2	14
		10–20	A2	16	3.0	3.5	11
		20–40	A3	18	3.3	3.1	10
		40–80	Bhg, Cgc	10	3.6	3.0	11
GON	Luvic Folic Planosol (Albic, Ruptic, Dystric, Siltic, Clayic)	–6.2–0	OFH	25	3.6	–	–
		0–5	A	20	2.9	17	23
		5–10	B	17	2.9	15	20
		10–20	B, 2B	17	3.0	12	15
		20–40	2B, 2Bg	12	3.3	14	21
		40–80	2Bg, 3Bg	7.8	3.5	23	61
		–3.0–0	OFH	23	3.1	24	81
		0–5	A	17	3.3	6.3	16
		5–10	Bh	17	3.5	4.3	13
		10–20	E	14	3.8	3.8	11
HOE	Albic Cutanic Alisol (Fragic, Abruptic, Alomic, Hyperdystric, Siltic)	20–40	Bt	10	3.8	4.6	8.9
		40–80	Btmx1	5.4	3.8	5.2	16

weighted to tree diameters, and bulked together. Stemflow volumes, obtained from individual sample trees, were upscaled on area basis using information of basal area.

Soil solution from the organic layer was sampled with four to six zero tension lysimeters. They consisted of a five cm high stainless steel box covered with a nylon mesh, installed just below the forest floor at four random locations per plot. Soil solution from the mineral soil was sampled with ceramic cup suction lysimeters, at three depths in the capillary zone (topsoil, subsoil and deeper mineral soil). Suction lysimeters were installed at three random locations per plot, each equipped with two or three samplers per depth. Samples were bulked to one composite sample per depth at every sampling event, using the entire collected volume.

2.3. Chemical analysis

Samples were treated and analysed as prescribed by the ICP Forests manual (ICP Forests, 2010). Quality control included analysis of control samples (blanks, reference material, replicates,...) and participation in the yearly ICP Forests water ring tests. Water samples (500 ml subsamples of each collected fraction) were kept cool during transport, stored in darkness at 4 °C and analysed within 48 h after sampling. pH (Multi 340i-glass electrode, WTW) and conductivity (Multi 340i-Tetracon®325, WTW) were measured on unfiltered subsamples. Concentrations of cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+) and anions (NO_3^- , SO_4^{2-} , Cl^-) were determined simultaneously using ion chromatography (IC) on filtered subsamples (0.45 µm). Total elemental concentrations of Al (Al_{tot}) were measured with a Liberty II plasma emission spectrometer (ICP).

2.4. Data handling

All field data (e.g., sample weights) and analytical results were subjected to a detailed quality check and validation procedure, according to the guidelines of the ICP Forests Working Group on Quality Assurance/Quality Control (Mosello et al., 2005). Throughfall and stemflow data showed only minor irregularities and validated data from all years were included in the data analysis. Soil solution data showed some inconsistencies and missing values as a result of drought periods and consequently low sampling volumes, especially during the first years after installation. These data were excluded from further analysis, reducing the time span of several data series.

Stand deposition was calculated as the sum of throughfall and stemflow deposition. Taking stand deposition as a variable instead of total deposition means that we did not correct for canopy exchange (canopy uptake of NH_4^+ , H^+ and NO_3^- , canopy leaching of Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} and weak acids,...). This way the many uncertainties and assumptions associated with the use of canopy budget models (Staelens et al., 2008) were avoided. Moreover, as stand deposition represents the amount of deposition that reached the forest floor, and as such directly affects soil solution chemistry, it is more relevant in the context of this study than total deposition. Stand deposition was corrected for inputs from marine sources (Stedman et al., 1990). Deposition of potentially acidifying compounds (ACID) was calculated as the sum of NO_3^- , NH_4^+ , SO_4^{2-} and Cl^- , corrected for the neutralizing effect of BC ($\text{BC} = \text{Ca}^{2+} + \text{K}^+ + \text{Mg}^{2+}$), according to UNECE (2004). Because water balance models have not yet been calibrated for the plots, the vertical water flux (the precipitation surplus) was estimated for each depth using the mass balance approach for Na^+ (Bailey et al., 2003), assuming negligible weathering of Na^+ from the mineral soil. This assumption is based on the low amount of extractable Na^+ (<100 mg kg^{-1}) in the mineral soils (De Vos and Cools, 2011), and

may result in a small but negligible underestimation of water fluxes. Annual soil fluxes of individual elements were then calculated by multiplying the water flux with mean annual soil solution concentrations at each depth. We assumed that elemental fluxes through the deeper mineral soil represented losses below the rooting zone. The ANC was obtained by subtracting the sum of SO_4^{2-} , NO_3^- and Cl^- from the sum of BC and Na^+ in mol_c. It was multiplied by the precipitation surplus to allow comparison with deposition fluxes. The BC/Al ratio for the mineral soil solution was calculated as the ratio of the sum of BC to Al_{tot} in mol_c, assuming that Al ions were entirely present as Al^{3+} .

2.5. Statistical analysis

The nonparametric Seasonal Mann–Kendall Test (Hirsch and Slack, 1984) was applied to detect monotonic trends in three-monthly aggregated data representing the four seasons (January–March,..., September–December) for stand deposition and soil solution fluxes. This test allows to detect possible effects of seasonality, unlike classical linear regression. Trends were evaluated by the significance of Sen's slope, which is the median change between years for all seasonal blocks (Sen, 1968). In order to ascertain whether SO_4^{2-} , NH_4^+ and NO_3^- were retained within the ecosystem, their mean annual output/input ratio was calculated for each soil depth. Differences between input (stand depositions) and output (soil solution fluxes at each depth) were evaluated using a paired *t*-test. Cross-site statistics were performed by means of ANOVA/Tukey's range test. We used two critical limits to evaluate whether soils showed chemical recovery and were protected against Al toxicity: ANC = 0 (Holmberg et al., 2001) and BC/Al ratio (BC/Al = 1.2 for *Pinus*; BC/Al = 0.6 for *Quercus* and *Fagus*) (Sverdrup and Warfvinge, 1993; UNECE, 2004).

3. Results

3.1. Trends in potentially acidifying depositions

Depositions of SO_4^{2-} and NH_4^+ significantly declined at all plots by 56–68% and 40–59% respectively (Table 3, Fig. 2). Depositions of NO_3^- decreased significantly in deciduous forest plots by 17–30%, but remained stable in coniferous forest plots. Depositions of N and S were highest in coniferous forest plots. $\text{NH}_4^+/\text{NO}_3^-$ ratios declined significantly at all locations from 2.44 to 1.90 (plot-averaged ratio). Depositions of BC decreased significantly at all plots by 19–41% and were highest in deciduous forest plots. Depositions of ACID decreased significantly at all plots by 45–74% and were highest in coniferous forest plots. We did not observe any relation between tree species or site and the rate of decrease in ACID depositions.

3.2. Trends in soil solution fluxes

Soil solution fluxes of SO_4^{2-} decreased significantly at most depths in all plots (Table 4, Fig. 3a–d). Fluxes of NH_4^+ through the organic layer decreased significantly in BRA, but remained stable at the other plots. In the mineral soil, fluxes of NH_4^+ were negligible. Soil solution fluxes of NO_3^- in coniferous forest plots decreased significantly in the mineral soil, but remained stable in the organic layer. In two deciduous forest plots (WIJ, HOE) fluxes of NO_3^- declined throughout the entire soil profile, but in GON this was confined to the deeper mineral soil. In the organic layer NO_3^- fluxes were lower in coniferous than deciduous forest plots. In the mineral soil, on the contrary, the lowest NO_3^- fluxes were observed in two deciduous forest plots (WIJ, HOE), while strongly elevated NO_3^- fluxes were found in GON. The decrease in the soil solution fluxes of

Table 3
Seasonal Mann–Kendall trends (1994–2010) for stand deposition with mean value in mm y^{−1} (stand precipitation) or mol_c ha^{−1} y^{−1} (NH₄⁺, NO₃[−], SO₄^{2−}, BC, ACID), mean ratio (NH₄⁺/NO₃[−]), letters (a–d) indicating groups of plots with comparable mean (*p* < 0.05) and Sen's slope with significance (*: *p* < 0.05, **: *p* < 0.01, ***: *p* < 0.001).

Plot	Stand precipitation		NH ₄ ⁺		NO ₃ [−]		NH ₄ ⁺ /NO ₃ [−] ratio		SO ₄ ^{2−}		BC		Acid	
	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope
RAV	636a		1901d	−69***	645b		2.96c	−0.09***	1229bc	−63***	733a	−11*	2995d	−127***
BRA	784b		1576c	−49***	709b		2.24b	−0.05***	1380c	−70***	966b	−25***	2593c	−93***
WIJ	712ab		1370bc	−72***	519a	−7*	2.67bc	−0.09***	1021 ab	−59***	1209bc	−19*	1763b	−120***
GON	657a		1155b	−49***	529a	−9*	2.18b	−0.06***	1212bc	−62***	1741d	−23**	1198a	−84***
HOE	743b		806a	−42***	521a	−12***	1.53a	−0.05***	869a	−53***	1400c	−47***	816a	−56***

SO₄^{2−} and NO₃[−] was accompanied by a decrease in BC and Al. Aluminium prevailed in the soil chemistry of the more sandy soils (RAV, BRA, WIJ), where the buffer system from the whole soil profile had entered the Al buffer range. Soil solution ANC increased significantly in three plots (BRA, WIJ, HOE), and remained nearly

stable in the other plots (Fig. 4). Mean ANC was below 0 except in the organic layer in HOE. In the mineral soil, BC/Al ratios decreased in three plots (RAV, WIJ, HOE) and remained nearly stable in the other plots (Fig. 5). Critical limits for BC/Al ratio were never exceeded in two deciduous forest plots (GON, HOE), but were

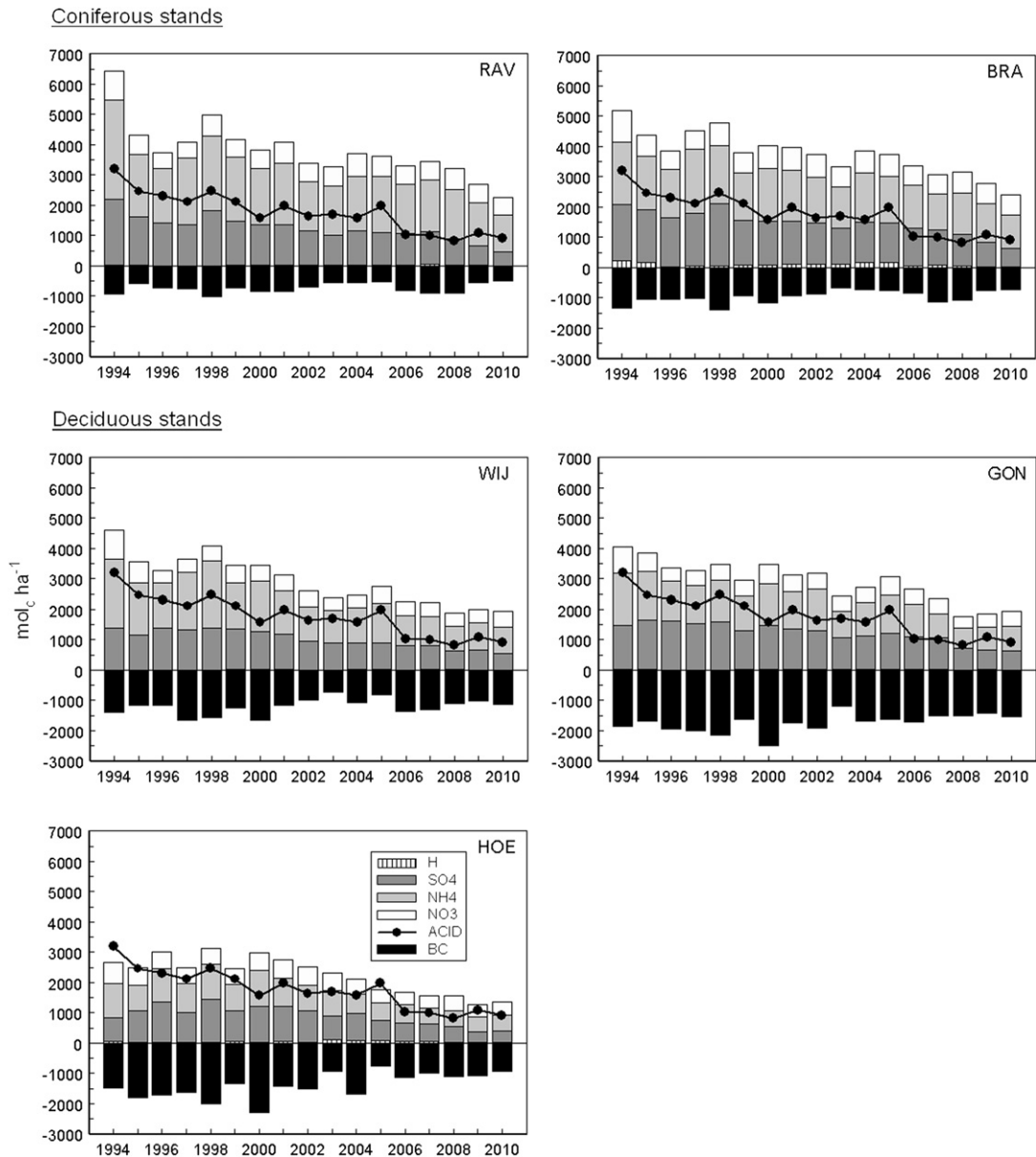


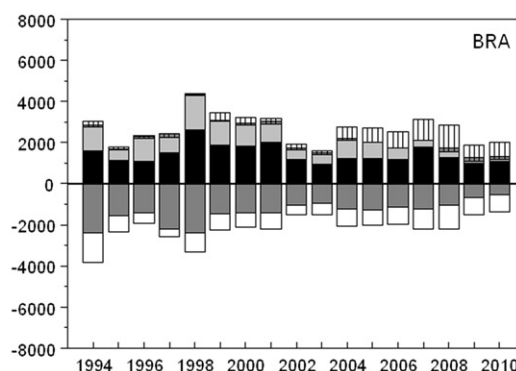
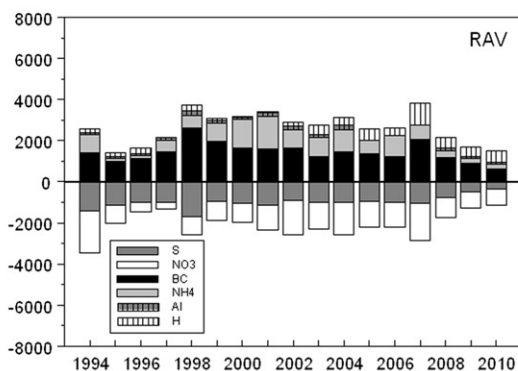
Fig. 2. Annual stand deposition (sea salt corrected) in mol_c ha^{−1} of BC (multiplied by −1), H⁺, SO₄^{2−}, NH₄⁺, NO₃[−] and ACID.

Table 4
Seasonal Mann–Kendall trends for soil solution fluxes with the examined period in years, mean value in mm y⁻¹ (precipitation surplus) or mol_c ha⁻¹ y⁻¹ (SO₄²⁻, NH₄⁺, NO₃⁻, BC, Al, H⁺, ANC), mean ratio (BC/Al), letters (a–d) indicating groups of plots with comparable mean ($p < 0.05$) and Sen's slope with significance (*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

Plot	Period	Depth (cm)	Prec. surplus		SO ₄ ²⁻		NH ₄ ⁺		NO ₃ ⁻		BC		Al		H ⁺		ANC		BC/Al	
			Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope	Mean	Slope
Organic layer																				
RAV	1994–2010		476a		997ab	–36***	709a		1113ab		1477a				336b	+26***	–1474a			
BRA	1994–2010		560ab		1383c	–64***	722ab	–64***	791a		1440a				405b	+41***	–1508a	+110***		
WIJ	2003–2010		662b		861a	–53**	379c		2590c	–192*	2979b				732c	–93**	–1158ab	+189**		
GON	1994–2010		469a		1268bc	–26*	495bc		1852d		3244b				973a	+5**	–573b			
HOE	1994–2010		508a		881a	–21*	352c		1373b	–30*	2806b				38a	+4***	+113c	+43**		
Topsoil																				
RAV	1997–2010	10–25	353ab		1111a	–67***	88a		1631b	–89**	887a	–80***	1811b		1155b		–2020a		0.49b	–0.04***
BRA	2002–2010	15–25	319ab		1127ab	–47*	10a		949a		720a	–52*	1006a	–135***	1101b		–1548ab	+92*	0.84ab	+0.07*
WIJ	2002–2010	10–20	351ab		914a	–61**	7a		756a	–160***	828a		786a	–76**	1016b	–112***	–1105bc	+161***	1.05ab	–0.05*
GON	1996–2010	10–20	317a		1492b	–77***	30a	+1**	2302c		3017b	–89***	982a	–34*	527a	+44***	–901c		3.15c	
HOE	2001–2010	10–15	418b	–21*	779a	–74***	6a		676a	–104***	1198a	–205***	590a	–46**	290a	–18*	–321d	+24*	1.99a	–0.19***
Subsoil																				
RAV	2002–2010	30–45	267a		874a		10a		1291ac	–141**	372a	–34**	2615d		330ab		–1874a	+158**	0.14a	–0.01***
BRA	1994–2010	30–55	280a		1487b	–76***	132b	–1**	1570bc	–130***	953b	–61***	1398bc	–83***	986c	–50***	–2205a	+173***	0.71a	
WIJ	1998–2010	45–70	250a		1105a	–59***	9a		1098ab	–167***	788ab	–105***	1872c	–140***	296ab	–20***	–1580a	+128***	0.37a	–0.03***
GON	1999–2010	25–40	326ab		1198ab		10a	+1***	1928c		2310c	–94**	961ab		449b		–902c		2.45b	–0.10***
HOE	1998–2010	20–30	415b	–18**	954a	–62***	33a		615a	–44***	1202b	–144***	550a		172a	–5*	–445c		2.43b	–0.27***
Deeper mineral soil																				
RAV	1994–2010	70–95	221ab	+14***	1353ab		4a		1365b	–51*	480a	–29***	2999d		171ab		–2465a		0.15a	–0.01***
BRA	1997–2010	70–90	300bc	–12***	1683b	–82***	3a		1120b	–104***	738a	–68***	2165c	–151***	488c	–28***	–2126a	+133***	0.35a	–0.02***
WIJ	2002–2010	75–110	197a	–8*	1178a	–69**	1a	–0.2*	351a	–64***	466a	–47***	1395b	–118***	138ab		–1319b	+115***	0.33a	–0.01**
GON	1994–2010	45–55	255ab	–9**	1389ab	–71***	6a		1321b	–84***	2009c	–104***	899ab	–67***	254b	–11***	–821bc		2.33b	+0.05**
HOE	1996–2010	35–55	377c		1091a	–60***	3a		504a	–28***	1225b	–89***	492a	–15*	116a		–433c	+18*	2.52b	–0.11**

a Organic layer

Coniferous stands



Deciduous stands

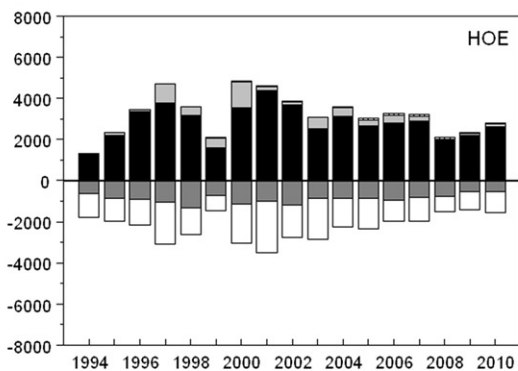
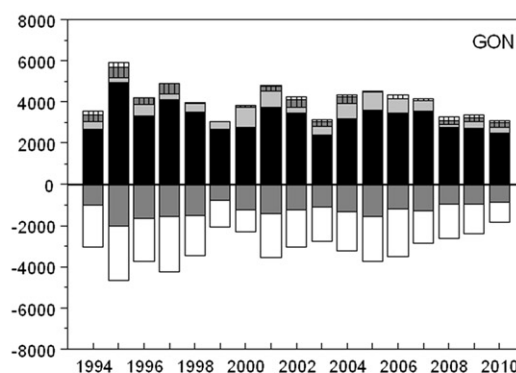
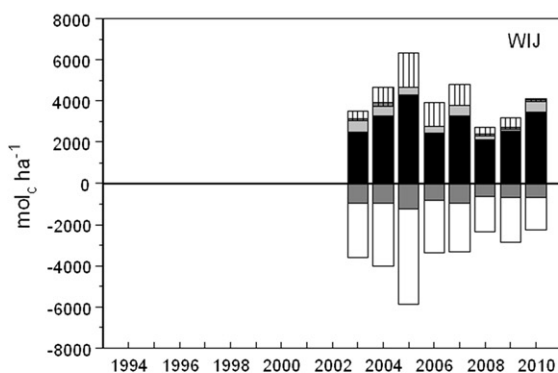


Fig. 3. Annual soil solution flux in $\text{mol}_c \text{ha}^{-1}$ for H^+ , Al , BC , NH_4^+ , SO_4^{2-} and NO_3^- in the organic layer (a), topsoil (b), subsoil (c) and deeper mineral soil (d). Values for SO_4^{2-} and NO_3^- were multiplied by (-1) to illustrate the charge balance (anions vs. cations).

permanently exceeded in the coniferous forest plots and in the subsoil and deeper mineral soil of one deciduous forest plot (WIJ).

3.3. Ion budgets of SO_4^{2-} , NO_3^- and NH_4^+

Coniferous forest plots showed significant retention of SO_4^{2-} in the upper soil layers, but outputs were not different from inputs in the deeper mineral soil (Table 5). In the deciduous forest plots, outputs of SO_4^{2-} were not different from inputs in the upper soil layers, but outputs of SO_4^{2-} were significantly higher than inputs in the deeper mineral soil at two plots (WIJ, HOE). The degree of inorganic N leaching showed considerable differences among the plots. In the organic layer, retention of N was observed in

coniferous forest plots, while deciduous forest plots showed significant net losses of N. One deciduous forest plot (GON) also showed significant net losses of N from the topsoil. Losses of N below the rooting zone varied from 16% (WIJ) to 76% (GON) of inorganic N inputs.

4. Discussion

4.1. Trends in potentially acidifying deposition

Depositions of N and S in Flanders range within the highest deposition classes defined for European Level II plots (Lorenz et al.,

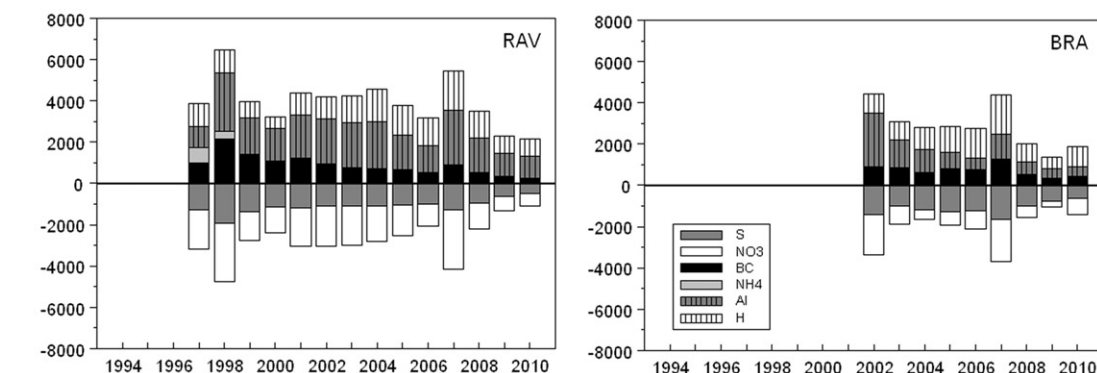
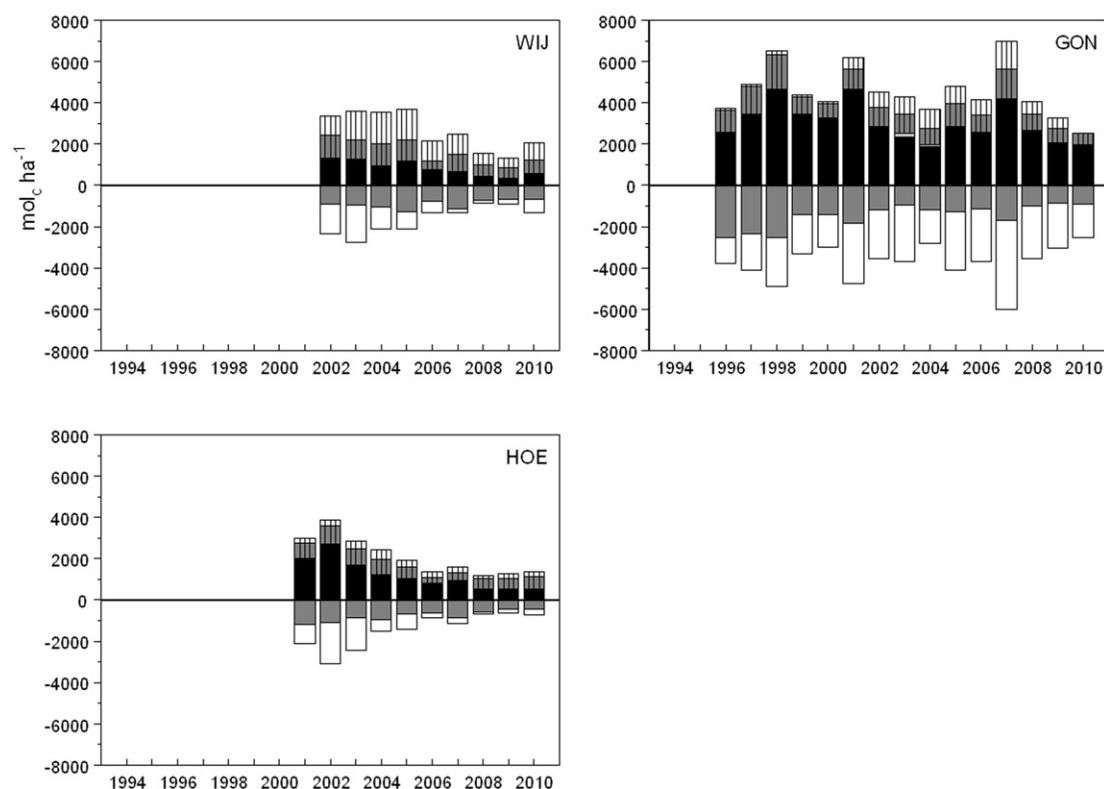
b TopsoilConiferous standsDeciduous stands

Fig. 3. (continued).

2008). This could be explained by the abundance of emission sources in this part of Europe, which is a densely populated, industrialized region, characterized by an important animal husbandry sector, and an intensively used road network. The observed deposition levels and decreasing trends of SO_4^{2-} , NH_4^+ and NO_3^- are comparable to results reported for Level II plots in neighbouring regions like southern Belgium (Jonard et al., 2012), northern France (van der Heijden et al., 2011) and southern UK (Vanguelova et al., 2010).

The strong decline of SO_4^{2-} depositions can be attributed to the measures taken by industry and power plants to reduce SO_2 emissions, which had already dropped below 1880 levels in 2010

(Mylona, 1996; VMM, 2011). The decrease of NH_4^+ can be attributed to NH_3 emission reductions by the agricultural sector (EEC, 1991) and a declining co-deposition with SO_4^{2-} (Cape et al., 1998). Depositions of NO_3^- diminished to a much lower extent or even remained stable. Traffic is responsible for 52–60% (1990–2010) of NO_x emissions in Flanders (VMM, 2011) and the highest NO_x depositions were observed near intensively used highways connecting the cities of Brussels, Antwerp and Ghent (MIRA, 2006). It appears that the effect of introducing low-emission vehicles in agreement with EU emission standards was counteracted by the increasing traffic density and the growing number of diesel vehicles.

C Subsoil

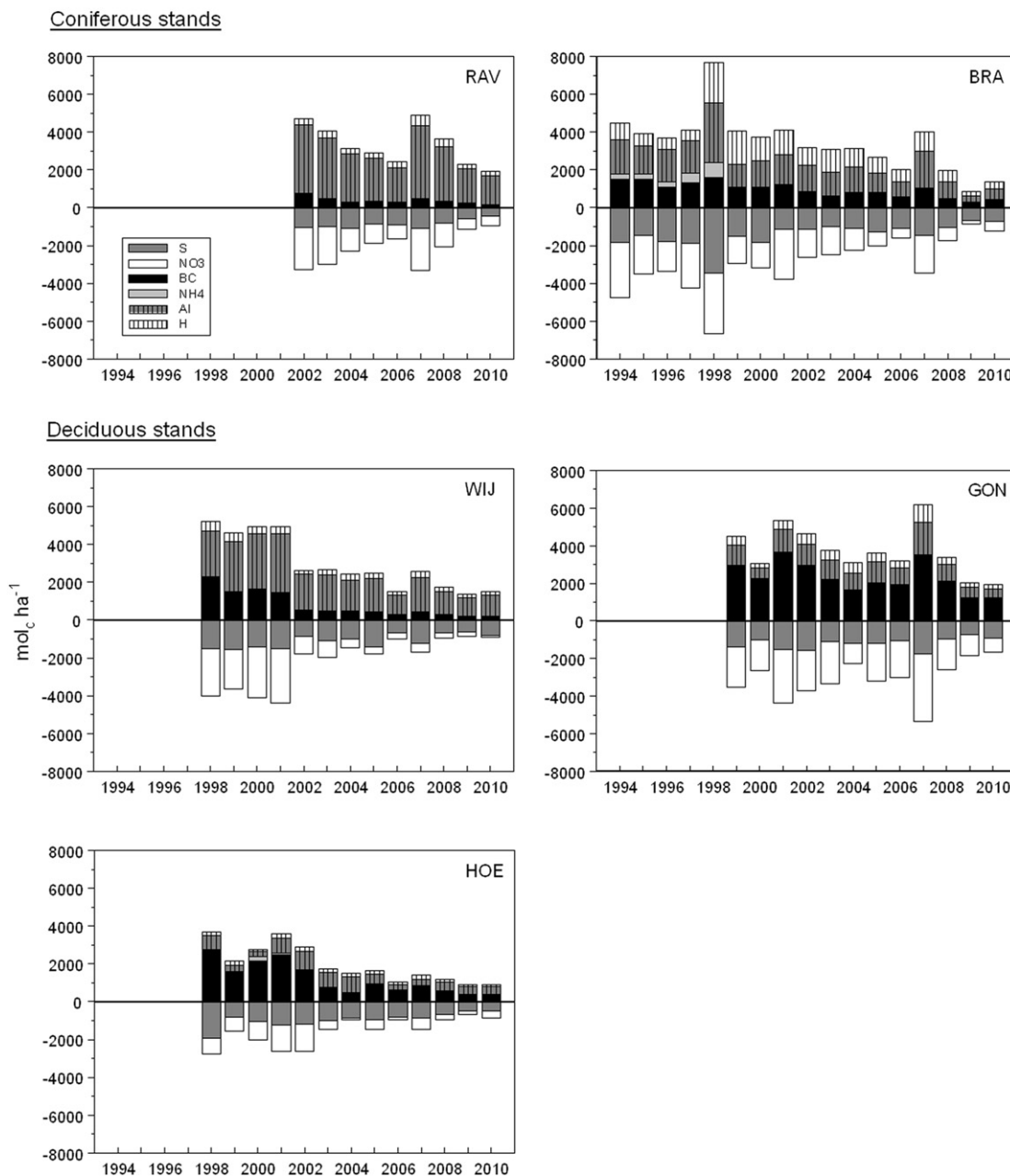


Fig. 3. (continued).

4.2. Effects on soil solution chemistry

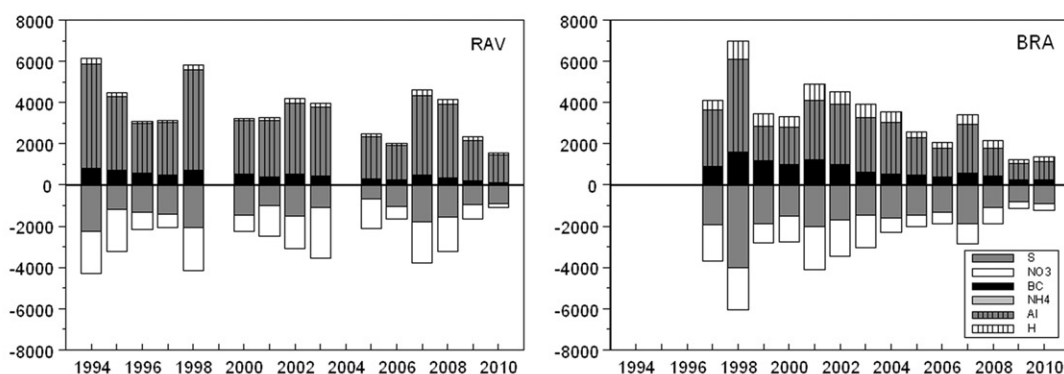
We observed that soil SO_4^{2-} fluxes decreased significantly in all plots, but to a lesser degree than we could expect from the observed decrease in S deposition, and we found a net release of SO_4^{2-} at two deciduous forest plots. Net release of SO_4^{2-} following a decline in S depositions has been reported in several European catchments (Prechtel et al., 2001), and may delay the de-acidification process by simultaneous release of H^+ (Karlun, 1997).

We found that fluxes of NO_3^- in the mineral soil decreased significantly at most soil depths in all plots, in reaction to declining inorganic N depositions. However, with an average leaching of $5\text{--}19 \text{ kg N ha}^{-1} \text{ y}^{-1}$ over the observation period, the

limit of $2\text{--}3 \text{ kg N ha}^{-1} \text{ y}^{-1}$ for elevated NO_3^- leaching was exceeded at all plots (Gundersen et al., 2006). Differences in NO_3^- leaching between the five plots could be explained by a combination of factors, like the local pollution climate (see Section 2.1), tree species (in general higher N uptake in deciduous species; Gundersen et al., 2009), soil C/N ratio related to litter quality and microbial activity (in general, higher leaching when C/N ratio decreases; MacDonald et al., 2002), site fertility (Kristensen et al., 2004) and by consequence also site history (in general higher degree of NO_3^- leaching in post-agricultural forests due to application of fertilizer; Callesen et al., 1999). In our study the role of site history is unclear, as the highest NO_3^- losses were observed at one of the old growth forest plots and the lowest at

d Deeper mineral soil

Coniferous stands



Deciduous stands

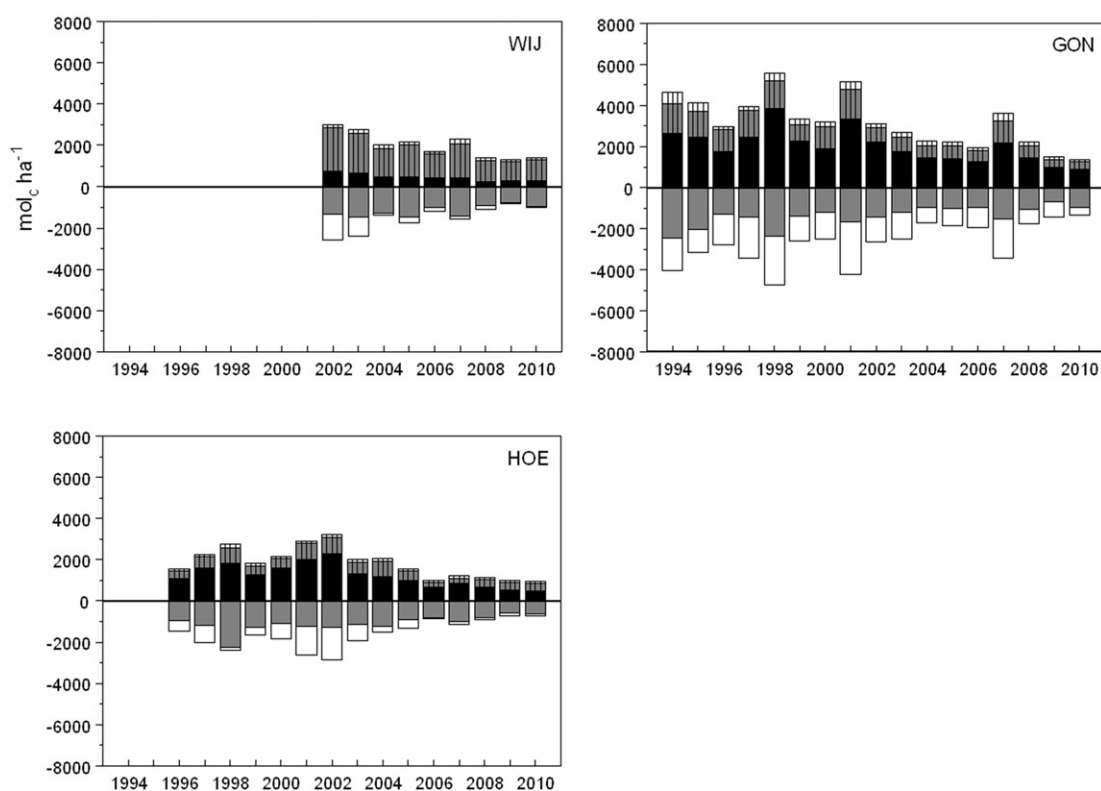


Fig. 3. (continued).

the plot on former arable land. The excessive losses of NO_3^- below the rooting zone in one deciduous forest plot (GON) are probably the result of more intense internal N processes, like humus disintegration mediated by drought periods (Eichhorn and Hüttermann, 1999).

We want to remark that it would be useful to calculate soil water fluxes based on detailed water balance models (as described in the ICP Forests manual; ICP Forests, 2010) and compare the outcome with the results for the sodium mass balance.

4.3. Critical loads and levels

As one of the species groups most sensitive to elevated air concentrations and depositions of N and S, epiphytic lichens and

mosses serve as good bio-indicators for air pollution (Conti and Cecchetti, 2001). Based on empirical research on lichens in forests, a critical load of $221 \text{ mol}_c \text{ N ha}^{-1} \text{ y}^{-1}$ was deduced for stand deposition (Fenn et al., 2008). In our study, stand depositions of inorganic nitrogen in 2010 varied between 977 and $1806 \text{ mol}_c \text{ N ha}^{-1} \text{ y}^{-1}$ at the five plots, which is 4–8 times higher than the critical load for sensitive lichen populations.

For ground vegetation in European temperate forests, an empirical critical load of $714\text{--}1071 \text{ mol}_c \text{ N ha}^{-1} \text{ y}^{-1}$ was deduced (UNECE, 2004). Above this level species diversity of ground vegetation may decrease by disappearance of species adapted to conditions of low nutrient availability. In 2010, the upper limit of this critical load for ground vegetation was respected in only one plot (HOE) and was still exceeded by 22–69% in the other four plots.

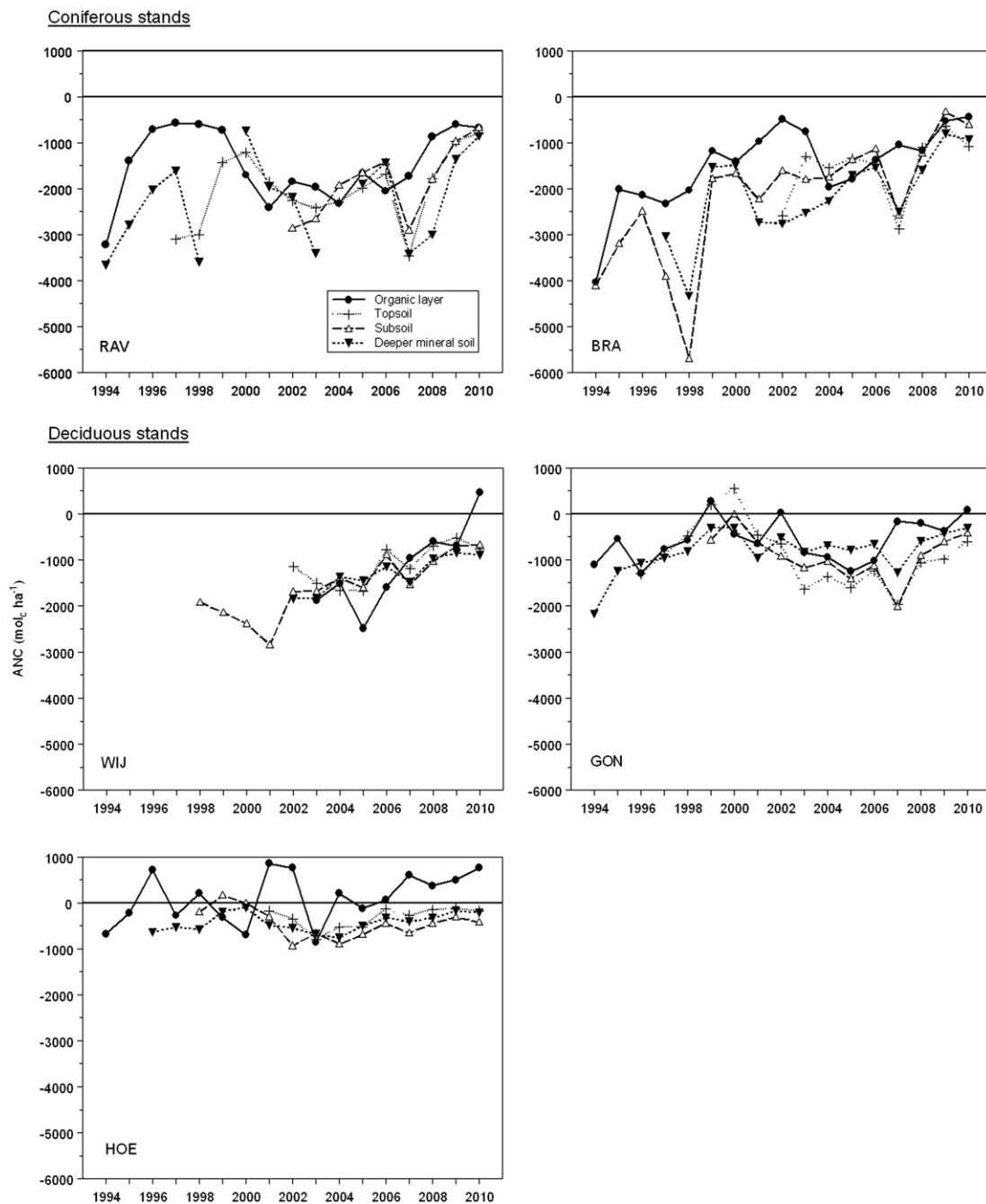


Fig. 4. Annual average ANC values (multiplied by precipitation surplus) in $\text{mol}_c \text{ ha}^{-1}$ for each soil depth. Positive values indicate recovery, negative values a proceeding of soil acidification.

Iost et al. (2012) demonstrated that the critical limits for N concentrations in soil solution are largely exceeded during most part of the year at all depths at the five plots. We observed that the critical limit for BC/Al ratio was exceeded continuously over the past 17 years in the coniferous forest plots and in the subsoil and deeper mineral soil of one deciduous forest plot (WIJ). In these plots trees may suffer more from root damage, which could lead to significant growth reductions. Two deciduous forest plots where the critical limit for BC/Al was respected (GON, HOE), receive lower ACID depositions and have soils with higher base saturation and

cation exchange capacity, which may explain the difference with the other plots.

We observed that ANC of soil solution remained <0 , except in the organic layer of one plot (HOE). This means that the acidification of forest soils in Flanders continued, despite a significant reduction of ACID depositions. The steady continuation of soil acidification, although at a slower pace compared to the start of the monitoring campaign, can be ascribed to a great extent to the simultaneous decrease of BC depositions and its impact on cation exchange processes (Alewell et al., 2000). Also, other soil buffering

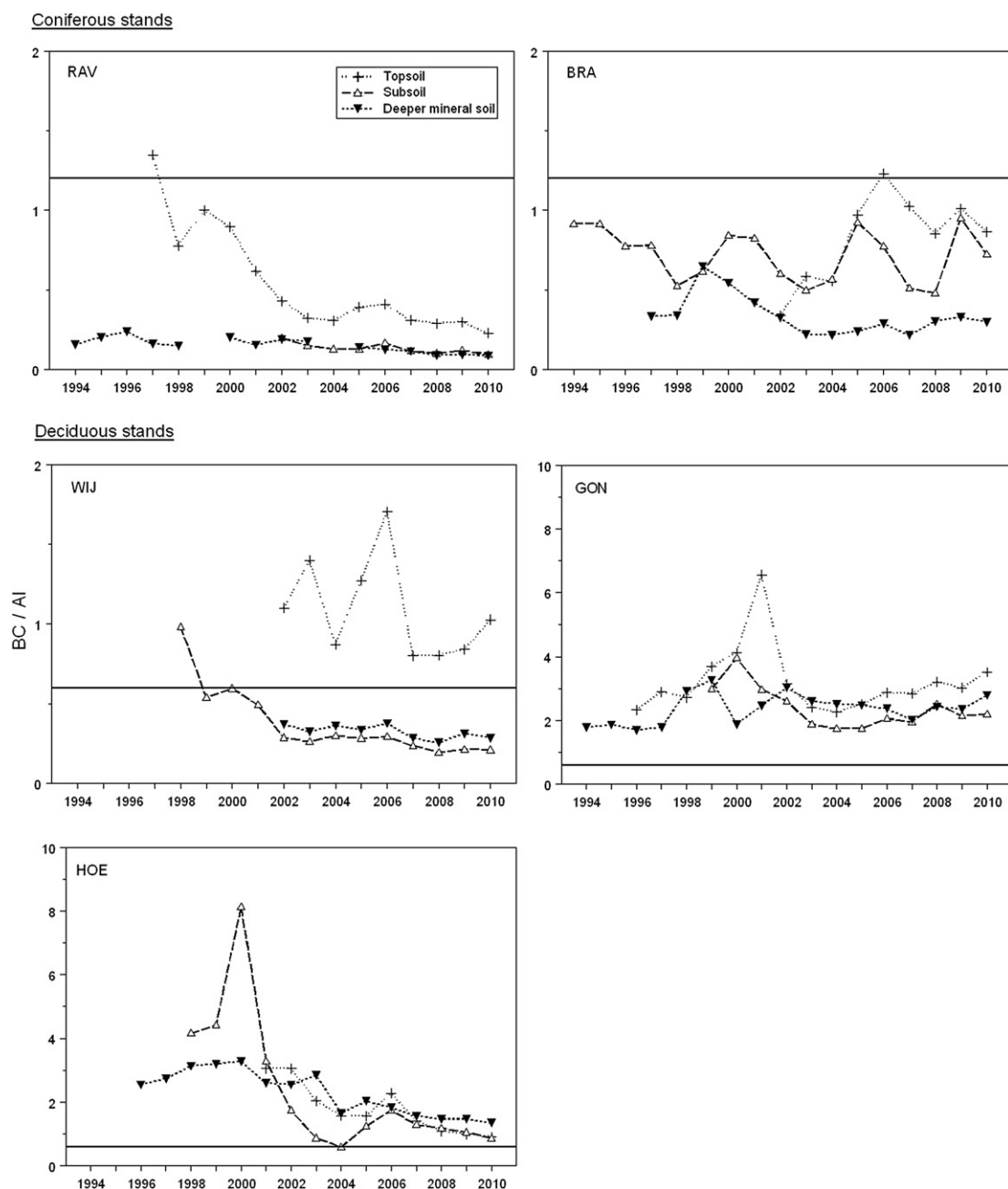


Fig. 5. Annual median BC/Al ratios for the mineral soil. Horizontal lines indicate critical limits (according to UNECE, 2004; Sverdrup and Warfvinge, 1993) for damage to fine roots, reduced tree stability, inhibited root growth and growth reductions of up to 80% of mean growth for beech/oak (0.6) and pine (1.2).

Table 5

Ion budget for stand depositions (inputs) and soil solution fluxes (outputs) expressed as % (outputs/inputs*100) for SO_4^{2-} (including inputs from sea salt) and $\text{NH}_4^+ + \text{NO}_3^-$ for the different soil depths. Between brackets the mean annual difference between inputs and outputs ($\text{mol}_e \text{ ha}^{-1} \text{ y}^{-1}$) is shown when significant (*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

Plot	Period	Organic layer		Topsoil		Subsoil		Deeper mineral soil	
		SO_4^{2-}	$\text{NH}_4^+ + \text{NO}_3^-$	SO_4^{2-}	$\text{NH}_4^+ + \text{NO}_3^-$	SO_4^{2-}	$\text{NH}_4^+ + \text{NO}_3^-$	SO_4^{2-}	$\text{NH}_4^+ + \text{NO}_3^-$
RAV	2002–2010	80 (198***)	84	93 (75*)	67 (727**)	84 (165***)	57 (943**)	124	58 (882**)
BRA	2002–2010	82 (231***)	60 (827***)	89	47 (1103**)	84 (207**)	48 (1076***)	108	41 (1214***)
WIJ	2003–2010	96	199 (1505**)	101	45 (784**)	104	27 (1066***)	129 (263**)	16 (1220***)
GON	1999–2010	101	146 (672***)	108	168 (924**)	104	129	102	76 (376*)
HOE	2001–2010	112	142 (509**)	100	54 (454*)	112 (76*)	46 (573***)	127 (179***)	37 (640***)

processes like SO_4^{2-} desorption (see Section 4.2), which are not well studied, further delay the start of recovery.

5. Conclusions

Potentially acidifying N and S depositions on Flemish forests decreased significantly between 1994 and 2010, but forest soils in Flanders are still in an unfavourable condition. Critical loads and levels were still exceeded and soil acidification due to human disturbances continued, because a simultaneous decline of BC depositions and short-term soil buffering processes like SO_4^{2-} desorption delay recovery.

Acknowledgements

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References

- Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen saturation in northern forest ecosystems: excess nitrogen from fossil fuel combustion may stress the biosphere. *BioScience* 39, 378–386.
- Alew, C., Manderscheid, B., Gerstberger, P., Matzner, E., 2000. Effects of reduced atmospheric deposition on soil solution chemistry and elemental contents of spruce needles in NE-Bavaria, Germany. *Journal of Plant Nutrition and Soil Science* 163, 509–516.
- Bailey, S.W., Buso, D.C., Likens, G.E., 2003. Implications of Sodium Mass Balance for interpreting the calcium cycle of a forested ecosystem. *Ecology* 84, 471–484.
- Callesen, I., Raulund-Rasmussen, K., Gundersen, P., Stryhn, H., 1999. Nitrate concentrations in soil solutions below Danish forests. *Forest Ecology and Management* 114, 71–82.
- Cape, J.N., Sheppard, L.J., Binnie, J., Dickinson, A.L., 1998. Enhancement of the dry deposition of sulphur dioxide to a forest in the presence of ammonia. *Atmospheric Environment* 32, 519–524.
- Conti, M.E., Cecchetti, G., 2001. Biological monitoring: lichens as bioindicators of air pollution assessment – a review. *Environmental Pollution* 114, 471–492.
- De Schrijver, A., Mertens, J., Geudens, G., Staelens, J., Campforts, E., Luysaert, S., De Temmerman, L., De Keersmaecker, L., De Neve, S., Verheyen, K., 2006. Acidification of forested podzols in North Belgium during the period 1950–2000. *Science of the Total Environment* 361, 189–195.
- De Vos, B., Cools, N., 2011. Second European Forest Soil Condition Report. In: Results of the Biosoil Soil Survey. INBO.R.2011.35, vol. I. Research Institute for Nature and Forest, Brussels.
- Driscoll, C.T., Driscoll, K.M., Mitchell, M.J., Raynal, D.J., 2003. Effects of acidic deposition on forest and aquatic ecosystems in New York State. *Environmental Pollution* 123, 327–336.
- Eichhorn, J., Hüttermann, A., 1999. Mechanisms of humus dynamics and nitrogen mineralisation. In: Rastin, N., Bauhus, J. (Eds.), *Going Underground – Ecological Studies in Forest Soils*. Research Signpost, Trivandrum, India, pp. 239–277.
- European Commission, 2001. Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on National Emission Ceilings for Certain Atmospheric Pollutants. <http://eur-lex.europa.eu>.
- European Economic Commission, 1991. Council Directive 91/676/EEC of 12 December 1991 Concerning the Protection of Waters Against Pollution Caused by Nitrates from Agricultural Sources. <http://eur-lex.europa.eu>.
- European Environment Agency, 2011. Ammonia (NH_3) emissions (APE 003) (APE 003) – Assessment published Dec 2011. <http://www.eea.europa.eu>.
- Fenn, M.E., Jovan, S., Yuan, F., Geiser, L., Meixner, T., Gimeno, B.S., 2008. Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. *Environmental Pollution* 155, 492–511.
- Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., Denier van der Gon, H., Frost, G.J., Heil, A., Kaiser, J.W., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J.F., Liousse, C., Masui, T., Meleux, F., Mieville, A., Ohara, T., Raut, J.C., Riahi, K., Schultz, M.G., Smith, S.J., Thompson, A., van Aardenne, A., van der Werf, G.R., van Vuuren, D.P., 2011. Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980–2010 period. *Climatic Change* 109, 163–190.
- Gundersen, P., Schmidt, I.K., Raulund-Rasmussen, K., 2006. Leaching of nitrate from temperate forests – effects of air pollution and forest management. *Environmental Reviews* 14, 1–57.
- Gundersen, P., Sevel, L., Christiansen, J.R., Vesterdal, L., Hansen, K., Bastrup-Birk, A., 2009. Do indicators of nitrogen retention and leaching differ between coniferous and broadleaved forests in Denmark? *Forest Ecology and Management* 258, 1137–1146.
- Hirsch, R.M., Slack, J.R., 1984. A nonparametric trend test for seasonal data with Serial Dependence. *Water Resources Research* 20, 727–732.
- Holmberg, M., Mulder, J., Posch, M., Starr, M., Forsius, M., Johansson, M., Bak, J., Ilvesniemi, H., Sverdrup, H., 2001. Critical loads of acidity for forest soils: tentative modifications. *Water, Air, and Soil Pollution: Focus* 1, 91–101.
- ICP Forests, 2010. Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE, ICP Forests, Hamburg. <http://icp-forests.org>.
- Iost, S., Rautio, P., Lindroos, A.J., 2012. Spatio-temporal trends in soil solution Bc/Al and N in relation to critical limits in European forest soils. *Water, Air, and Soil Pollution* 223, 1467–1479.
- IUSS Working Group WRB, 2007. World Reference Base for Soil Resources 2006, First Update 2007. World Soil Resources Report No. 103. FAO, Rome.
- Jonard, M., Legout, A., Nicolas, M., Dambrine, E., Nys, C., Ulrich, E., Van der Perre, R., Ponette, Q., 2012. Deterioration of tree vitality despite a sharp decline in acid deposition: a long-term regional perspective. *Global Change Biology* 18, 711–725.
- Karlton, E., 1997. Modelling SO_4^{2-} surface complexation on variable charge minerals: I. H^+ and SO_4^{2-} exchange under different solution conditions. *European Journal of Soil Science* 48, 483–491.
- Kristensen, H.L., Gundersen, P., Callesen, I., Reinds, G.J., 2004. Throughfall nitrogen deposition has different impacts on soil solution nitrate concentration in European coniferous and deciduous forests. *Ecosystems* 7, 180–192.
- Lorenz, M., Nagel, H.-D., Granke, O., Kraft, P., 2008. Critical loads and their exceedances at intensive forest monitoring sites in Europe. *Environmental Pollution* 155, 426–435.
- MacDonald, J.A., Dise, N.B., Matzner, E., Armbruster, M., Gundersen, P., Forsius, M., 2002. Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests. *Global Change Biology* 8, 1028–1033.
- MIRA, 2006. Milieuraapport Vlaanderen, Achtergronddocument 2006, Verzuring, van Avermaet P., van Hooste H., Overloop S., Vlaamse Milieumaatschappij. <http://www.milieuraapport.be>.
- Monteith, D.T., Stoddard, J.L., Evans, C.D., De Wit, H.A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopáček, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450, 537–540.
- Mosello, R., Amoriello, M., Amoriello, T., Arisci, S., Carcano, A., Clarke, N., Derome, J., Derome, K., Koenig, N., Tartari, G., Ulrich, E., 2005. Validation of chemical analyses of atmospheric deposition in forested European sites. *Journal of Limnology* 64, 93–102.
- Mylona, S., 1996. Sulphur dioxide emissions in Europe 1880–1991 and their effect on sulphur concentrations and depositions. *Tellus B* 48, 662–689.
- Neirynck, J., Van Ranst, E., Roskams, P., Lust, N., 2002. Impact of decreasing throughfall depositions on soil solution chemistry at coniferous monitoring sites in northern Belgium. *Forest Ecology and Management* 160, 127–142.
- Prechtel, A., Alewell, C., Armbruster, M., Bittersohl, J., Cullen, J.M., Evans, C.D., Helliwell, R., Kopáček, J., Marchetto, A., Matzner, E., Meesenburg, H., Moldan, F., Moritz, K., Vesely, J., Wright, R.F., 2001. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Sciences* 5, 311–325.
- Ronse, A., De Temmerman, L., Guns, M., De Borger, R., 1988. Evolution of acidity, organic matter content, and CEC in uncultivated soils of North Belgium during the past 25 years. *Soil Science* 146, 453–460.
- Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of American Statistical Association* 63, 1379–1389.
- Sevenant, M., Menschaert, J., Couvreur, M., Ronse, A., Heyn, M., Janssen, J., Antrop, M., Geypens, M., Hermy, M., De Blust, G., 2002. Ecodistricten: Ruimtelijke eenheden voor gebiedsgericht milieubeleid in Vlaanderen. Studieopdracht in het kader van actie 134 van het Vlaamse Milieubeleidsplan 1997–2001. In opdracht van het Ministerie van de Vlaamse Gemeenschap, Administratie Milieu, Natuur, Land- en Waterbeheer.
- Staelens, J., Houle, D., De Schrijver, A., Neirynck, J., Verheyen, K., 2008. Calculating dry deposition and canopy exchange with the canopy budget model: review of assumptions and application to two deciduous forests. *Water, Air, and Soil Pollution* 191, 149–169.
- Stedman, J.R., Heyes, C.J., Irwin, J.G., 1990. A comparison of bulk and wet-only precipitation collectors at rural sites in the United Kingdom. *Water, Air, and Soil Pollution* 52, 377–395.
- Sverdrup, H., Warfvinge, P., 1993. Effect of Soil Acidification on Growth of Trees and Plants as Expressed by the (Ca+Mg+K)/Al Ratio. Reports in Ecology and Environmental Engineering 1993-2. Lund University, Lund.
- Ulrich, B., Mayer, R., Khanna, P.K., 1979. Deposition von Luftverunreinigungen und ihre Auswirkungen in Waldökosystemen im Solling. Schriften Forstl. Fakult. Göttingen.
- UNECE, 2004. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels; and Air Pollution Effects, Risks and Trends. <http://www.rivm.nl>.
- van der Heijden, G., Legout, A., Nicolas, M., Ulrich, E., Johnson, D.W., Dambrine, E., 2011. Long-term sustainability of forest ecosystems on sandstone in the Vosges Mountains (France) facing atmospheric deposition and silvicultural change. *Forest Ecology and Management* 261, 730–740.
- Vanguelova, E.L., Benham, S., Pitman, R., Moffat, A.J., Broadmeadow, M., Nisbet, T., Durrant, D., Barsoum, N., Wilkinson, M., Bocheau, F., Hutchings, T., Broadmeadow, S., Crow, P., Taylor, P., Durrant Houston, T., 2010. Chemical fluxes

- in time through forest ecosystems in the UK — Soil response to pollution recovery. *Environmental Pollution* 158, 1857–1869.
- Van Steertegem, M. (Ed.), 2012. MIRA Indicatorrapport 2011. Milieurapport Vlaanderen. Vlaamse Milieumaatschappij. <http://www.milieurapport.be>.
- VMM, 2011. Lozingen in de lucht 1990–2010. <http://www.vmm.be>.
- Weathers, K.C., Cadenasso, M.L., Pickett, S.T.A., 2001. Forest edges as nutrient and pollutant concentrators: potential synergisms between fragmentation, forest canopies, and the atmosphere. *Conservation Biology* 15, 1506–1514.